

RECENT ADVANCES IN COAL/HEAVY OIL CO-PROCESSING

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ABSTRACT

The second half of a 36 month U.S. DOE Bench Scale Co-Processing Program (Contract No. DE-AC22-94PC91036) with combined processing of coal and petroleum resid at Hydrocarbon Technologies, Inc. has been completed. This program is jointly funded by the U.S. Department of Energy, Mitsui SRC and Hydrocarbon Technologies, Inc. Experimental activities undertaken include the use of a bituminous coal with supported catalyst, the use of a fully dispersed catalyst, the use of a commercially available supported catalyst, and the use of a simulated water-emulsified oil feed with syngas serving as a partial source of hydrogen. During the last half of this program four bench operations were performed covering 78 days of continuous operation.

The use of a bituminous coal (Illinois No. 6) as opposed to the sub-bituminous coal used throughout this program (McKinley Mine) results in comparable process performance and economics. The dispersed catalyst loading used was 1000-2000 wppm Fe and 50-100 wppm Mo. The replacement of the supported catalyst with a finely dispersed catalyst allows a larger thermal volume and excellent contact between the feed and the catalyst particles. Process performance at equivalent reactor operating conditions for supported catalyst and the dispersed catalyst systems used are comparable. However, on an economic basis the dispersed catalyst is more economical than the supported catalyst. The alternate supported catalyst selected was Davison GR-14, which performed extremely well and gave some of the highest conversions and distillate yields. The use of a simulated water/oil emulsion was also tested using syngas as a source of hydrogen with a dispersed catalyst. This demonstrated that CO and water can be used to replace part of the hydrogen feed for coal/oil co-processing using a fully dispersed Molybdenum catalyst with a small decrease in overall performance.

PROCESS DESCRIPTION

These tests were performed in continuous pilot plant scale unit present at HTI. This unit is capable of operation with up to four stages as fully ebullated reactors or as backmixed reactors. All these test were performed as two stage operations.

The coal/oil slurry is premixed offline and charged to a feed tank on a periodic basis. The slurry feed is pumped through both reactors with or without interstage separation. Interstage separation, if used, removes the light oils and the gases from the first reactor so that the second reactor is more efficiently used to upgrade only the remaining heavy material. The effluent from the second reactor is separated in a hot separator. The overhead from the hot separator is sent to a cold separator and separated into a vent gas stream and a separator overhead stream (SOH). The vent gases are metered, sampled, and sent to flare, and the SOH is collected. The second stage hot separator overhead stream can also be sent directly to an in-line hydrotreater for further upgrading and heteroatom removal. For co-processing and heavy oil upgrading, the bottoms material from the hot separator is separated offline in a batch vacuum distillation into a vacuum still overhead stream (VSOH) and a vacuum still bottoms stream (VSB). These streams are then analyzed. Part of the VSOH is used as a process oil in the buffer pumps for the first and second stage reactors. For coal liquefaction, the bottoms material from the hot separator is separated offline in a pressure filter into a pressure filter liquid (PFL) and a pressure filter solid (PFS). These streams are then analyzed. Part of the PFL is used as a process

oil in the buffer pumps for the first and second stage reactors, and part of the PFL is used as the slurry oil for the coal and fed back to the reactors.

EXPERIMENTAL

The single best condition for coal/oil co-processing from each of the last four pilot plant tests will be discussed. The relative reactor conditions are presented in *Table 1*. The relative reactor temperature is presented as a difference from a base temperature in degrees Celsius. The relative space velocity is presented as a ratio to a base space velocity. The relative reactor severity is based upon the residence time in the reactors and the reactor temperatures. It is presented as a ratio to a base reactor severity. The reactor severity is the best basis for comparison of different test conditions as two tests performed with different space velocities and reactor temperatures but identical reactor severities should have comparable performance. Based on relative reactor severity, all four cases should be very comparable. The one that stands out slightly is BSU-6 Condition 4; this case has a relative severity of 1.10. This higher severity would improve the performance results for this condition; however, this is countered by the high catalyst age (885 wt feed / wt catalyst) which would decrease the performance results. The distillate yield will be discussed in terms of naphtha, mid distillate and heavy distillate yield. Naphtha is defined as the C_4 -177°C fraction, mid distillate as the 177-343°C fraction, and the heavy distillate as the 343-524°C fraction.

DISCUSSION OF RESULTS

Comparing BSU-2 Condition 3 with BSU-3 Condition 3 shows the effect of changing the coal type from sub-bituminous to bituminous. The coal conversion for BSU-3 is higher due to both the higher reactor severity and the change in coal. This would also lead to higher resid conversion and potentially lighter products except that BSU-3 also has a higher catalyst age (536 as compared to 441 wt feed / wt catalyst) which would lead to lower resid conversion and heavier products. These two points tend to negate each other so that this should be a reasonable comparison. The bituminous coal has a higher resid conversion, 89.6 as compared to 89.2 W% maf ff, and a higher distillate yield, 79.1 as compared to 78.8 W% maf ff. However, these increases are very slight and the actual performance should be considered equivalent. The product distribution for these two conditions is different. The mid-distillate yield is nearly the same, 36.32 W% maf ff for the sub-bituminous coal and 35.32 W% maf ff for the bituminous coal, but the naphtha and heavy distillate yields are very different. The bituminous coal shows a strong shift in favor of the naphtha yield, from 15.07 to 18.92 W% maf ff, and away from the heavy distillate, from 27.37 W% maf ff to 24.89 W% maf ff. While the overall resid conversion and distillate yield are very comparable for these two catalysts, the bituminous coal shows a higher conversion of heavy distillates to light distillates. This helps contribute to the bituminous coal having a higher hydrogen consumption, 4.5 as compared to 4.1 W% maf ff.

Comparing BSU-2 Condition 3 with BSU-6 Condition 4 shows the effect of changing the supported catalyst type from AKZO AO-60 to Davison GR-14, a commercially available catalyst. The coal conversion for BSU-6 is higher due to the higher reactor severity. This would also lead to higher resid conversion and lighter products except that BSU-6 also has a higher catalyst age (885 as compared to 441 wt feed / wt catalyst) which would lead to lower resid conversion and heavier products. These two points tend to negate each other so that this should be a reasonable comparison. The alternate supported catalyst has a higher resid conversion, 89.8 as compared to 89.2 W% maf ff, and a higher distillate yield, 79.1 as compared to 78.8 W% maf ff. However, these increases are very slight and the actual performance should be considered equivalent. The product distribution for these two conditions is very different. The mid-distillate yield is nearly the same, 36.32 W% maf ff for the AKZO catalyst and 37.34 W% maf ff for the Davison catalyst, but the naphtha and heavy distillate yields are very different. The Davison catalyst shows a very strong shift in favor of the naphtha yield, from 15.07 to 21.62 W% maf ff, and away from the heavy distillate, from 27.37 W% maf ff to 20.11 W% maf ff. While the overall resid conversion and distillate yield are very comparable for these two catalysts, the

Davison catalyst shows a higher conversion of heavy distillates to light distillates. This helps contribute to the Davison catalyst having a higher hydrogen consumption, 4.8 as compared to 4.1 W% maf ff.

Comparing BSU-4 Condition 5 and BSU-6 Condition 4 shows the effect of replacing the supported catalyst with a fully dispersed catalyst system for coal/oil co-processing. BSU-6 used Davison GR-14 as the supported catalyst. This is the highest activity supported catalyst identified during this program and used for co-processing. The supported catalyst test was performed at a higher reactor severity than the dispersed catalyst test, 1.10 as compared to 0.90. This accounts for the slightly higher coal conversion for the supported catalyst test, 95.7 as compared to 95.4 W% maf ff, and for a significant amount of the higher 524+C resid conversion for the supported catalyst test, 89.8 as compared to 84.2 W% maf ff. At identical reactor severities the dispersed catalyst should be nearly equal in coal and resid conversion to the supported catalyst. Of more interest is the product yields generated. One significant difference is the much lower total gas make for the dispersed catalyst, 12.0 as compared to 16.6 W% maf ff. The dispersed catalyst also has a lower water yield than the supported catalyst, 4.9 as compared to 5.3 W% maf ff. The differences in these yields is a significant contribution to the dispersed catalyst having a lower hydrogen consumption, 4.0 as compared to 4.8 W% maf ff. Along with a lower water yield, the dispersed catalyst has a higher CO and CO₂ yield, total of 0.9 as compared to a total of 0.4 W% maf ff. From this it can be seen that the dispersed catalyst has a higher bias in promoting oxygen to form CO and CO₂ as opposed to water. This is a beneficial point as it lowers the hydrogen consumption. The dispersed catalyst results in a lower total distillate yield, as would be expected by the lower total resid conversion. For the dispersed catalyst, the naphtha and mid distillate yield are both lower while the heavy distillate yield actually increases slightly, by 3 W% maf ff. This slight shifting of material to the heavier product fraction can largely be attributed to the difference in reactor severities, an at equal reactor severities the dispersed and supported catalyst systems should have very comparable performance.

BSU-5 Condition 2 was performed using syngas (43 V% CO and 57 V% H₂) in the first reactor and hydrogen in the second reactor. The water / oil / coal emulsion was simulated by directly injecting water into the high pressure section of the feed lines before the first stage reactor. Comparing BSU-4 Condition 5 and BSU-5 Condition 2 shows the effect of the use of syngas and the change in the dispersed catalyst (from 2059 wppm Fe and 103 wppm Mo to 206 wppm Mo). BSU-5 shows a higher distillate yield and resid conversion even though it also has a slightly lower coal conversion. The distribution of liquid products also shows an increase in the lighter fractions at the expense of the heavier fraction. On this basis, the syngas system performed very well. The syngas was also performed with a higher quantity of CO into the first reactor (70 V%) and at higher relative space velocities (1.4 and 1.9). Either of these changes had a detrimental impact on the performance. Increasing the concentration of syngas to the first reactor caused little change to the resid conversion, 86.1 W% maf ff, but caused the distillate yield to drop to 74.7 W% maf ff. Further increasing the relative space velocity to 1.9 caused the resid conversion to drop to 77.1 W% maf ff and the distillate yield to drop to 69.4 W%.

For BSU-3, 4, 5, & 6 an in-line hydrotreater was used to further upgrade the hot separator overhead stream from both the first and second stage reactors. The second stage overhead was fed directly to the hydrotreater at temperature and with a hydrogen partial pressure from the second stage reactor effluent. The first stage overhead was collected and then pumped back up to pressure and fed to the hydrotreater. The product quality from the hydrotreater was not substantially different for any of these tests. All have sulfur and nitrogen contents less than 70 wppm and H/C atomic ratios of 2.0. This demonstrates that the SOH product from the dispersed catalyst, from syngas or from the bituminous coal is no more difficult to hydrotreat than that from the supported catalyst with sub-bituminous coal.

ECONOMICS

An economic comparison for these tests is presented in *Table 2*. The system derived by BECHTEL to evaluate the economics of a coal liquefaction or co-processing process is based on the calculation of an equivalent crude oil price. This calculated number is the price that crude oil would need to sell at to make the process profitable with a 15% rate of return on the equity. It provides an easy benchmark for comparison among different tests. The results are presented for three different scenarios. The first is with a constant feed rate of 6,400 t/d. The second scenario is for the case of maximum throughput through reactors with maximum diameter assuming the same superficial gas velocity. The first two scenarios are both for stand alone grassroots facilities. The last scenario assumes that the plant would be integrated into an existing refinery substantially reducing plant investment. The last two scenarios are the most realistic ones. In a grass-roots co-processing complex, constant throughput comparison shows that the equivalent crude oil price is in the range of \$25 to \$27/bbl. Increasing the throughput to a maximum rate lowers this price to \$22 to \$24/bbl. When the process is integrated into a refinery this price can be further lowered to approximately \$18/bbl. The use of either a bituminous or a sub-bituminous coal is an economic standoff. The use of the alternate supported catalyst or the dispersed catalyst is also an economic standoff. No discussion will be included here on the economic evaluation of BSU-05 as the assumptions being used are still being evaluated.

CONCLUSIONS

While performance characteristics and yields varied among these operating conditions the economic evaluation was surprisingly even. This demonstrates that at present there are a variety of systems that are all equally economically feasible for the commercialization of the co-processing technology. The system that would be most economic would be dependent on the individual factors of the plant being built; proximity to a bituminous or sub-bituminous coal, operation with supported or dispersed catalyst, or operation with different supported catalysts. The major impact on the process economics are that the plant be designed for maximum throughput and integrated, if possible, into an existing refinery. This brings the equivalent crude oil price to approximately \$18/bbl.

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TABLE 1: Comparison of Dispersed and Supported Catalyst Operating Conditions, Performance and Yields

Test ID / Condition Purpose	BSU-02 / 3 Supported Cat Temp. Staging	BSU-3 / 3 Supported Cat. Illinois No.6 Coal	BSU-4 / 5 Dispersed Catalyst	BSU-5 / 2 Syngas with Emulsified Feed	BSU-6 / 4 Alternate Supported Cat.
Experimental Conditions					
Coal	McKinley	Illinois No. 6	McKinley	McKinley	McKinley
Coal Type	Sub-Bituminous	Bituminous	Sub-Bituminous	Sub-Bituminous	Sub-Bituminous
Oil	Hondo VB	Hondo VB	Hondo VB	Hondo VB	Hondo VB
Supported Catalyst	AKZO AO-60	AKZO AO-60	None	None	Davison GR14
Dispersed GELCAT, wppm Fe	none	none	2059	none	none
Dispersed Molyvan-L, wppm Mo	none	none	103	206	none
Relative Reactor Conditions					
Stage 1 Temp, °C (T _r +T)	-19.4	-2.2	+4.9	-11.0	+8.5
Stage 2 Temp, °C (T _r +T)	+14.4	+13.9	+12.3	+7.0	+17.5
Space Velocity, (SV/SV _r)	1.6	1.9	2.4	1.4	2.3
Reactor Severity, (Sev/Sev _r)	0.93	.99	0.90	.89	1.10
Catalyst Age, (wt feed / wt catalyst)	441	536	na	na	885
Coal Concentration, W% mf	33	33	33	33	33
Process Performance, W% maf ff					
Hydrogen Consumption	4.1	4.5	4.0	4.7	4.8
Coal Conversion	94.3	96.1	95.4	94.8	95.7
Resid (524+C) Conversion	89.2	89.6	84.2	85.8	89.8
C4-524C Distillate Yield	78.8	79.1	74.8	77.2	79.1
Normalized Yields, W% maf ff					
C ₁ -C ₃ Gases	6.23	7.15	6.51	5.83	7.33
Naphtha (C ₄ Gases - 177 °C)	15.07	18.92	17.29	18.58	21.62
Mid Distillate (177 - 343 °C)	36.32	35.32	34.45	37.92	37.34
Heavy Distillate (343 - 524 °C)	27.37	24.89	23.11	20.70	20.11
524+ °C	7.68	7.83	12.29	10.73	7.47
Unconverted Coal / Coke	1.76	1.19	1.49	1.62	1.40
Water	5.61	3.72	4.86	5.18	5.31
CO	0.17	0.15	0.34	0.03	0.15
CO ₂	0.04	0.09	0.52	0.05	0.30
NH ₃	0.58	0.85	0.47	0.64	0.74
H ₂ S	3.25	4.39	2.67	2.91	3.04

TABLE 2: Economic Evaluation				
Test ID / Condition Purpose	BSU-2 / 3 Supported Cat. Temp. Staging	BSU-3 / 3 Supported Cat. Illinois No.6 Coal	BSU-4 / 5 Dispersed Catalyst	BSU-6 / 4 Alternate Supported Cat.
Yield, bbl product/ton feed	4.95	4.97	4.70	5.02
H ₂ consumption, scf/bbl product	3,150	3,370	3,180	3,510
Feed Rate = 6,400 t/d				
Total Plant Investment, \$MM	1,160	1,198	1,126	1,176
Equivalent Crude Oil Price, \$/bbl	25.79	26.19	26.16	25.76
Maximum Throughput				
Feed Rate, t/d	6,400	9,640	10,580	9,640
Total Plant Investment, \$MM	1,160	1,625	1,633	1,595
Equivalent Crude Oil Price, \$/bbl	25.79	23.20	22.59	22.91
Refinery Integration				
Total Plant Investment, \$MM	593	595	566	597
Equivalent Crude Oil Price, \$/bbl	18.00	17.94	18.06	17.95